PESTICIDE SURFACE WATER QUALITY REPORT

NOVEMBER 2015 SAMPLING EVENT

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Summary

As part of the South Florida Water Management District's (SFWMD) quarterly ambient monitoring program, unfiltered surface water grab samples were collected November 16 to November 19, 2015, and analyzed for over 70 pesticides and/or products of their degradation.

The herbicides 2,4-D, ametryn, atrazine, bentazon, diuron, metolachlor, metribuzin, along with the insecticide imidacloprid, were detected in one or more of these surface water samples. No harmful impacts are expected from the detected pesticides.

The compounds and concentrations found are typical of those expected from an area of intensive historical and contemporary agricultural activity.

Background and Methods

The SFWMD pesticide monitoring network includes stations designated in the Everglades Settlement Agreement, the Lake Okeechobee Protection Act Permit, and the non-Everglades Construction Project (non-ECP) permit. The canals and marshes depicted in **Figure 1** are protected as Florida Administrative Code (F.A.C.) 62-302 Class III (fishable and swimmable) waters, while Lake Okeechobee and a segment of the Caloosahatchee River are protected as a Class I drinking water supply. Arthur R. Marshall Loxahatchee National Wildlife Refuge/Water Conservation Area 1 (WCA-1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards apply. Surface water and sediment are sampled quarterly and semiannually or annually, respectively, upstream at each structure identified in the permit or agreement.

Seventy-two pesticides and degradation products were analyzed in samples from 25 of the network 26 sites (**Figure 1**). The analytes, their respective method detection limits (MDLs), and practical quantitation limits (PQLs) are listed in **Table 1**. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee, Florida. Analytical method details can be found at the following location: http://www.dep.state.fl.us/labs/cgi-bin/sop/chemsop.asp.

To evaluate the potential impacts on aquatic life, the observed concentration is compared to the appropriate criterion outlined in F.A.C. 62-302.530. If a pesticide compound is not specifically listed, acute and chronic toxicity criterion are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, using the lowest technical grade effective concentration 50 (EC_{50}) or lethal concentration 50 (LC_{50}) reported in the summarized literature for the species significant to the indigenous aquatic community (F.A.C. 62-302.200). Each pesticide's description and possible uses and sites of application described herein are taken from Hartley and Kidd (1987). This summary covers surface water samples collected from November 16 to November 19, 2015.

Results

At least one pesticide was detected in surface water at 23 of the 25 sites. The non-ECP permit requires sampling at S142 only during discharge or flow events. For this sampling event, no sample was obtained due to the lack of discharge at the time of sample collection. All of these compounds have previously been detected in this monitoring program.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible acute and chronic toxicity and environmental fate impacts are reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

2,4-D: 2,4-D is a selective systemic herbicide used for the post-emergence control of annual and perennial broad leaf weeds in terrestrial (grassland, established turf, sugarcane, rice, and on non-crop areas) as well as aquatic areas. Environmental fate and toxicity data in **Tables 3 and 4** indicate that 2,4-D (1) has minimum loss from soil by surface adsorption, with a moderate loss by leaching and surface solution; (2) is slightly toxic to mammals and relatively non-toxic to fish; and (3) does not bioaccumulate significantly. The highest 2,4-D residue was detected at S140 (0.13 µg/L) (**Table 2**). Using these criteria, this observed level should not have an acute or chronic effect on fish or aquatic invertebrates.

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations greater than (>) 10 µg/L (Verschueren, 1983). Environmental fate and toxicity data in **Tables 3 and 4** indicate that ametryn (1) is moderately lost from soil by leaching, surface adsorption, and in surface solution;

(2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 14.1 milligrams per liter (mg/L) for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.018 to 0.033 µg/L (**Table 2**). Using these criteria, these observed surface water concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf, lawn grasses, and non-crop areas. Environmental fate and toxicity data in **Tables 3 and 4** indicate that atrazine (1) has a large potential for loss from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 76 mg/L for carp, 16 mg/L for perch, and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 µg/L for bluegill and fathead minnow, respectively (Verschueren, 1983). The draft ambient aquatic life water quality criterion identifies a one-hour average concentration that does not exceed 1,500 µg/L more than once every three years on the average (United States Environmental Protection Agency [U.S. EPA], 2003a). The atrazine surface water concentrations found in this sampling event at 10 of the 23 sampling locations, ranged from 0.010 to 0.15 µg/L (**Table 2**). Using these criteria, these observed surface water concentrations should not have an acute or chronic detrimental impact on fish or invertebrates.

Bentazon: Bentazon is a contact herbicide used for post-emergence control of many annual broad-leaved weeds in beans, peas, rice, and established turf. Environmental fate and toxicity data in **Tables 3 and 4** indicate that bentazon (1) is easily lost from soil by leaching, with moderate loss from surface solution, and minimum loss by surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The highest detected concentration of 0.36 µg/L at S8 (**Table 2**), is below any level that would have an acute or chronic detrimental impact on fish or aquatic invertebrates.

Diuron: Diuron is a selective, systemic terrestrial herbicide registered for use on sugarcane, bananas, and citrus. Environmental fate and toxicity data in **Tables 3 and 4** indicate that diuron (1) is easily lost from soil in surface solution, with moderate loss from leaching or surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96-hour LC_{50} of 25 mg/L for guppies (Hartley and Kidd, 1987). Crustaceans are affected at lower concentrations with a 48-hour LC_{50} of 1.4 mg/L for water fleas and a 96-hour LC_{50} of 0.7 mg/L for water shrimp (Verschueren, 1983). Most algal effects occur at concentrations > 10 µg/L (Verschueren, 1983). The only surface water concentration of diuron found during this sampling event was 0.0042 µg/L at S140 (**Table 2**). Using these criteria, this concentration should not have an acute, harmful impact on fish, aquatic invertebrates, or algae.

Imidacloprid: Imidacloprid is a systemic insecticide registered for use on a variety of row crops and turf grass applications as well as for flea control. Environmental fate and toxicity data in **Tables 3 and 4** indicate that imidacloprid (1) is soluble in water; (2) is slightly toxic to mammals and

relatively non-toxic to fish; and (3) does not bioconcentrate significantly. The highest detected concentration of 0.0076 μg/L at S140 (**Table 2**) is below any level that would have an acute or chronic detrimental impact on fish or aquatic invertebrates.

Metolachlor: Metolachlor is a selective herbicide used on potatoes, sugarcane, and some vegetables. Environmental fate and toxicity data in **Tables 3 and 4** indicate that metolachlor (1) has a large potential for loss due to leaching and a medium potential for loss in surface solution and due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Metolachlor is non-toxic to birds (Lyman et al., 1990). The only surface water concentration found in this sampling event (0.057 μg/L at S191) (**Table 2**) is orders of magnitude below the calculated chronic toxicity level. Using these criteria, this observed level should not have a harmful effect on fish or aquatic invertebrates.

Metribuzin: Metribuzin is a selective systemic herbicide used on a variety of crops including potatoes, tomatoes, sugarcane, and peas. Environmental fate and toxicity data in **Tables 3 and 4** indicate that metribuzin (1) has a large potential for loss due to leaching, a medium potential for loss in surface solution, and a small potential for loss due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The only concentration of metribuzin detected was 0.023 μg/L at S140 (**Table 2**). Using these criteria, this surface water concentration should not have an acute impact on fish or aquatic invertebrates.

Quality Assurance Evaluation

No pesticide analytes were detected in the field blanks performed at S191, S177, S31, and S8. All of the 25 collected samples were shipped and all bottles were received.

Figure 1. South Florida Water Management District Pesticide Monitoring Network.

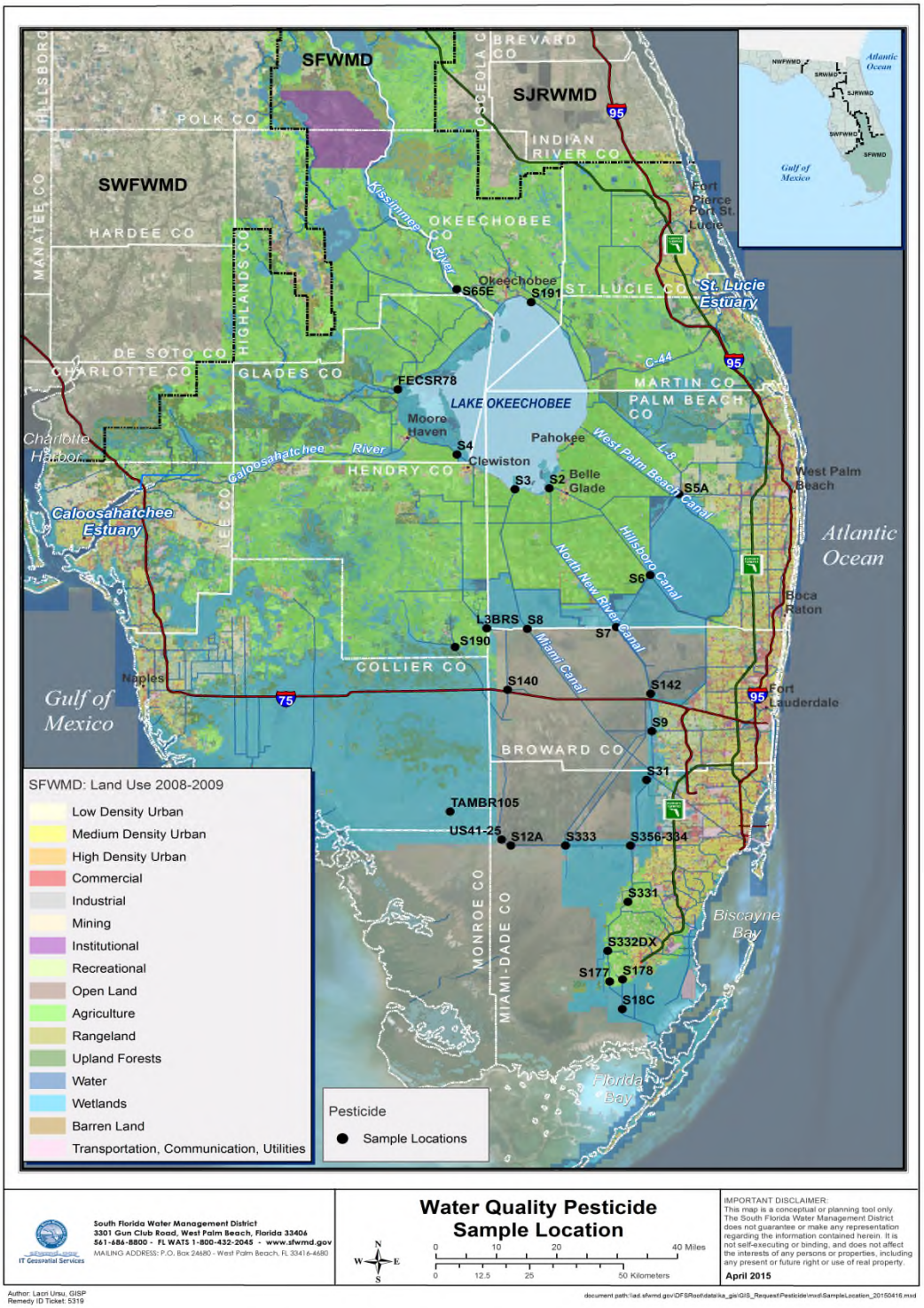

Table 1. Method detection limits (MDLs) and practical quantitation limits (PQLs) for November 2015 sampling event.

Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)	Pesticide or metabolite	Water: range of MDLs - PQLs (µg/L)
2,4-D	0.002 - 0.01	endrin	0.0037 - 0.016
2,4,5-T	0.002 - 0.01	endrin aldehyde	0.0037 - 0.016
2,4,5-TP (silvex)	0.002 - 0.01	ethion	0.0094 - 0.04
acifluorfen	0.002 - 0.01	ethoprop	0.0047 - 0.02
alachlor	0.056 - 0.24	fenamiphos	0.028 - 0.12
aldrin	0.0019 - 0.008	fonofos	0.0094 - 0.04
ametryn	0.0094 - 0.04	heptachlor	0.0019 - 0.008
atrazine	0.0094 - 0.04	heptachlor epoxide	0.0019 - 0.008
atrazine desethyl	0.0094 - 0.04	hexazinone	0.028 - 0.12
atrazine desisopropyl	0.0094 - 0.04	imidacloprid	0.004 - 0.016
azinphos methyl (guthion)	0.019 - 0.08	linuron	0.004 - 0.02
bentazon	0.002 - 0.01	malathion	0.0094 - 0.04
α-BHC (alpha)	0.0019 - 0.008	metalaxyl	0.037 - 0.16
β-BHC (beta)	0.0019 - 0.008	methoxychlor	0.0094 - 0.04
δ-BHC (delta)	0.0019 - 0.008	metolachlor	0.056 - 0.24
γ-BHC (gamma) (lindane)	0.0019 - 0.008	metribuzin	0.019 - 0.08
bromacil	0.037 - 0.16	mevinphos	0.0094 - 0.04
butylate	0.019 - 0.08	mirex	0.0037 - 0.016
carbophenothion (trithion)	0.0056 - 0.024	naled	0.037 - 0.16
chlordane	0.019 - 0.08	norflurazon	0.028 - 0.12
chlorothalonil	0.0075 - 0.032	parathion ethyl	0.019 - 0.08
chlorpyrifos ethyl	0.0094 - 0.04	parathion methyl	0.0094 - 0.04
chlorpyrifos methyl	0.0094 - 0.04	PCB-1016	0.019 - 0.08
cypermethrin	0.011 - 0.048	PCB-1221	0.019 - 0.08
DDD-P,P’	0.0037 - 0.016	PCB-1232	0.019 - 0.08
DDE-P,P’	0.0037 - 0.016	PCB-1242	0.019 - 0.08
DDT-P,P’	0.0037 - 0.016	PCB-1248	0.019 - 0.08
demeton	0.022 - 0.096	PCB-1254	0.019 - 0.08
diazinon	0.0094 - 0.04	PCB-1260	0.019 - 0.08
dicofol (kelthane)	0.022 - 0.096	permethrin	0.0094 - 0.04
dieldrin	0.0019 - 0.008	phorate	0.0047 - 0.02
disulfoton	0.0047 - 0.02	prometon	0.019 - 0.08
diuron	0.002 - 0.01	prometryn	0.019 - 0.08
α-endosulfan (alpha)	0.0019 - 0.016	simazine	0.0094 - 0.04
β-endosulfan (beta)	0.0019 - 0.016	toxaphene	0.094 - 0.4
endosulfan sulfate	0.0037 - 0.016	trifluralin	0.0075 - 0.032

Table 2. Summary of pesticide residues (µg/L) detected above the method detection limit in surface water samples collected by SFWMD in November 2015.

Date	Location	Flow	2,4-D	ametryn	atrazine	bentazon	diuron	imidacloprid	metolachlor	metribuzin	Number of compounds detected at location
11/16/2015	S177	N	-	-	-	0.0071 I	-	-	-	-	1
	S178	N	-	-	-	0.12	-	-	-	-	1
	S18C	N	-	-	-	0.016	-	-	-	-	1
	S331	N	-	-	0.010 I	0.023	-	-	-	-	2
	S332DX	Y	-	-	-	0.022	-	-	-	-	1
11/17/2015	S12A	Y	-	-	-	0.10	-	-	-	-	1
	S31	N	-	-	-	0.090	-	-	-	-	1
	S356-334	Y	-	-	-	0.017	-	-	-	-	1
	S333	Y	-	-	-	0.15	-	-	-	-	1
	US41-25	Y	-	-	-	0.025	-	-	-	-	1
	TAMBR105	Y	-	-	-	-	-	-	-	-	0
11/18/2015	FECSR78	Y	-	-	-	0.0030 I	-	-	-	-	1
	L3BRS	N	0.0025 I	-	-	0.022	-	-	-	-	2
	S140	N	0.13	-	-	0.016	0.0042 I	0.0076 I	-	0.023 I	5
	S191	N	0.010	-	-	0.0039 I	-	-	0.057 I	-	3
	S2	N	0.0046 I	-	0.15	0.0086 I	-	-	-	-	3
	S3	N	-	-	0.14	-	-	-	-	-	1
	S4	N	0.018	0.018 I	0.084	0.022	-	-	-	-	4
	S65E	Y	0.0063 I *	-	0.035 I *	0.023 *	-	0.0074 I *	-	-	4
	S8	N	-	0.018 I	0.031 I	0.36	-	-	-	-	3
	S190	N	-	-	-	-	-	-	-	-	0
11/19/2015	S6	N	0.061	0.033 I	0.03 I	0.10	-	-	-	-	4
	S7	N	0.0039 I	0.028 I	0.03 I	0.24	-	-	-	-	4
	S5A	N	0.086	-	0.15	0.0065 I	-	-	-	-	3
	S9	N	0.034	-	0.055	0.05	-	-	-	-	3
Total number of compound detections			10	4	10	22	1	2	1	1	51

N = no, Y = yes, R = reverse, ND = not discernable; - = result is below the method detection limit
I = value reported is less than the practical quantitation limit, and greater than or equal to the method detection limit
* = value is the average of replicate samples

Table 3. Selected properties of pesticides detected during the November 2015 sampling event.

Common Name	Surface Water Standards F.A.C. 62-302 (µg/L)	Acute Oral LD_{50} For Rats (mg/Kg) (1)	Bioconcentration Factor (2)	Volatility from Water (2)	Soil Conservation Service (SCS) rating (3)			K_{oc} (mL/g) (3, 4)	Soil Half-life (days) (3, 4)	Water Solubility (WS) (mg/L) (3, 4)	U.S. EPA Carcinogenic Potential (5)
					LE	SA	SS				
2,4-D (acid)	(100)	375	13	I	M	S	M	20	10	890	D
ametryn	-	1,110	33	I	M	M	M	300	60	185	D
atrazine	-	3,080	86	I	L	M	L	100	60	33	C
bentazon	-	1,100	19	I	L	S	M	34	20	500	C
diuron	-	3,400	75	I	M	M	L	480	90	42	D
imidacloprid	-	424(6)	18	I	-	-	-	178(6)	520(6)	510(6)	E
metolachlor	-	2,780	18	I	L	M	M	200	90	530	C
metribuzin	-	2,200	11	I	L	S	M	41	30	1,220	D

- = No data available

FDEP F.A.C. 62-302 surface water standards (8/2013) for Class III waters except Class I noted in ( )

Bioconcentration Factor (BCF) calculated as BCF = $10^{\wedge(2.71 - 0.564 \log WS)}$ (2)

Volatility from water: R = rapid, I = insignificant, S = significant

SCS ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large (L), medium (M), small (S), or extra small (XS)

B2 = probable human carcinogen; C = possible human carcinogen; D = not classified; E = evidence of non-carcinogen for humans (5)

(1) Hartley and Kidd (1987)
(2) Lyman, et al. (1990)
(3) Goss and Wauchope (1992)
(4) Montgomery (1993)
(5) U.S. EPA (1996)
(6) U.S. EPA (1994a)

Table 4. Toxicity of pesticides detected during the November 2015 sampling event to freshwater aquatic invertebrates and fishes (µg/L).

	Water Flea *(Daphnia magna)*			Fathead Minnow # *(Pimephales promelas)*			Bluegill *(Lepomis macrochirus)*			Largemouth Bass *(Micropterus salmoides)*			Rainbow Trout # *(Oncorthynchus mykiss)*			Channel Catfish *(Ictgalurus punctatus)*		
Pesticide Common Name	48 hour EC_{50}	Acute Toxicity (*)	Chronic Toxicity (*)	96 hour LC_{50}	Acute Toxicity	Chronic Toxicity	96 hour LC_{50}	Acute Toxicity	Chronic Toxicity	96 hour LC_{50}	Acute Toxicity	Chronic Toxicity	96 hour LC_{50}	Acute Toxicity	Chronic Toxicity	96 hour LC_{50}	Acute Toxicity	Chronic Toxicity
2,4-D	25,000 (3)	8,333	1,250	133,000 (3)	44,333	6,650	180,000 (4)	60,000	9,000	-	-	-	100,000 (1)	33,333	5,000	-	-	-
							900 (48 hr) (2)	-	-				110,000 (3)	36,667	5,500			
ametryn	28,000 (3)	9,333	1,400	16,000 (5)	5,333	800	4,100 (1)	1,367	205	-	-	-	8,800 (1)	2,933	440	-	-	-
													3,600 (5)	1,200	180			
atrazine	6,900 (3)	2,300	345	15,000 (3)	5,000	750	16,000 (1)	5,333	800	-	-	-	8,800 (1)	2,933	440	7,600 (1)	2,533	380
													5,300 (6)	1,767	265			
bentazon	>100,000 (10)	33,333	5,000	-	-	-	>100,000 (10)	33,333	5,000	-	-	-	>100,000 (10)	33,333	5,000	-	-	-
diuron	1,400 (3)	467	70	14,200 (3)	4,733	710	5,900 (1)	1,967	295	-	-	-	5,600 (1)	1,867	280	-	-	-
	1,400 (8)	467	70	14,000 (8)	4,667	700												
imidacloprid	85,200 (9)	28,400	4,260	-	-	-	-	-	-	-	-	-	83,000 (9)	27,667	4,150	-	-	-
metolachlor	23,500 (3)	7,833	1,175	-	-	-	15,000 (1)	5,000	750	-	-	-	2,000 (1)	667	100	4,900 (3)	1,633	245
metribuzin	4,200 (3)	1,400	210	-	-	-	80,000 (1)	26,667	4,000	-	-	-	64,000 (1)	21,333	3,200	100,000 (3)	33,333	5,000
	4,200 (7)	1,400	210				75,900 (7)	25,300	3,795				76,770 (7)	25,590	3,839			

- = No data available

(*) F.A.C. 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC_{50} is the lowest value which has been determined for a species significant to the indigenous aquatic community.

(#) Species is not indigenous. Information is given for comparison purposes only.

(1) Hartley and Kidd (1987)
(2) Verschueren (1983)
(3) U.S. EPA (1991)
(4) Mayer and Ellersieck (1986)
(5) U.S. EPA (2005)
(6) U.S. EPA (2006)
(7) U.S. EPA (1998)
(8) U.S. EPA (2003b)
(9) U.S. EPA (1994a)
(10) U.S. EPA (1994b)

Glossary

Bioconcentration Factor: The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

EC_{50}: A concentration necessary for 50 percent of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.

Henry's law constant (H): Relates the concentration of a compound in the gas phase to its concentration in the liquid phase. The constant is calculated from the formula: $H = P_{vp}/S$ where P_{vp} is pressure in atmospheres and S is solubility in moles/meter^3 for a compound.

K_{oc}: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

LC_{50}: A concentration which is lethal to 50 percent of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.

LD_{50}: The dosage which is lethal to 50 percent of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.

Method Detection Limits (MDLs): The minimum concentration of an analyte that can be detected with 99 percent confidence of its presence in the sample matrix.

Practical Quantitation Limits (PQLs): The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQLs are further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15 percent. In general, PQLs are 2 to 5 times larger than the MDLs.

Soil or water half-life: The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

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